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QUANTUM MECHANICAL CALCULATION OF LIGHT METAL DIATOMIC
HYDRIDES, OXIDES, AND HALIDES

ABSTRACT

An abbreviated discussion is given of certain quantum mechanical calculations completed, in course, or beginning for small molecules. The development of theory, computer programs, and extensive calculations on atoms is outlined. This includes polarizability studies, relativistic calculations and extensive configuration interaction for a few atomic systems.

Results for diatomic molecules in minimal LCAO-MO-SCF approximation is reviewed, and the gradual extension of this effort first to double-zeta LCAO-MO-SCF results and presently to true Hartree-Fock accuracy by the matrix method is discussed. The range of diatomic molecule-systems treated, the related molecular properties calculated, and physical or chemical interpretation efforts are outlined. A generalized Hartree-Fock method has been tried out on Li_2 and H_2 , and promises considerable improvement. A resume is also given of certain polyatomic calculations carried out. This latter effort includes limited (or minimal) basis set calculations for certain linear triatomic molecules, methane, and one-center expansion calculations for AH_n hydrides, all within the self-consistent-field procedure. Calculations on the hydrogen molecule using a lengthy James-Coolidge expansion, have been carried to within a few kaysers of experiment for the ground and certain few excited states.

A. THEORETICAL DEVELOPMENTS AND CALCULATIONS ON ATOMS*

The theoretical formulation of the matrix solution of the Hartree-Fock equations for open-shell configurations was studied extensively in this period. The generality of the allowed open-shell cases was progressively extended or simplified and machine programs (in fact a sequence of such programs) were constructed to carry out such calculations. The theory, numerical methods, and programming were unusually closely correlated as a unit. An extensive table of open-shell vector-coupling coefficients was also obtained for cases involving several open-shells of different symmetries. Using these programs, extensive calculations of wave functions and energies to Hartree-Fock accuracy were obtained for first and second row atoms (in collaboration with others). Extensive calculations were also carried out for $1s^2 2s^m 2p^n$ states of N, N^+ , O, and O^+ ; ground and several excited states of Al, Cu^+ , and Cu; ground states of Mo and Mo^+ ; and the ground states of K^+ , K, and Ca. A careful and extensive study of the K-shell and X-ray transition probabilities of some Neon-like and Argon-like ions was carried out using calculated SCF wave functions. Still in progress are calculations on transition probabilities and wave functions for certain relevant states. Complementary to this effort, and continuing, is the programme to numerically solve the Hartree-Fock equations for atoms. This latter effort has led to the development of newer and superior numerical methods for this old problem.

The fully-coupled self-consistent-field equations for a closed shell atom in an electric field have also been formulated, coded, and solved. The dipole polarizabilities of He-like, Be-like, Ne-like, and Mg-like ions have thus been calculated in good agreement with experiment (where known, except for H⁻).

A relativistic self-consistent-field theory has been developed for closed shell atoms. In this theory the many-electron Hamiltonian is taken as the sum of Dirac Hamiltonians, plus the usual Coulombic repulsion terms between electrons. This Hamiltonian is thus employed in a matrix SCF method using as basis functions Slater-Type-Orbitals with non-integer principle quantum numbers. The usual Breit interaction operator is used as the relativistic interaction term, and is treated in first-order perturbation. The program constructed using this method was employed to make relativistic calculations on He, Be, and Ne (all 1S_0).

Several calculations considerably beyond Hartree-Fock approximation have also been carried out. Thus "correlated" orbital calculations have been carried out for He-like systems and, in a most comprehensive series of calculations, the ground-state wave functions of He, Li, and Be were approximated by a superposition of configurations with 35 terms for He and up to 55 terms for Be. Isoelectronic series were also studied for this series of atoms.

*Theoretical work on atoms is also included here because of the frequent role atomic calculations have played as a preliminary to the corresponding molecular calculations, directly or indirectly.

B. VERY ACCURATE CALCULATIONS ON THE HYDROGEN MOLECULE

A number of important results for the ground and certain excited states of H_2 have been obtained. These calculations employed a James-Coolidge type expansion to represent the electronic wave function. Initial calculations for $H_2(X^1\Sigma_g^+)$ employed up to a 40-term expansion and together with a Hartree-Fock wave function gave the R variation of the "correlation" energy. These calculations were later extended to permit up to 80 terms in the expansion, and the James-Coolidge technique was generalized to permit the correct asymptotic behavior at large R. Thus calculations were made on the $X^1\Sigma_g^+$, $b^3\Sigma_u^+$, $C^1\Pi_u$, and $B^1\Sigma_u^+$ states of H_2 and the first two $^1\Sigma^+$ states of HeH^+ . The resulting wave functions were then used to obtain nuclear motion and relativistic corrections and the final energies are within a few kayers (cm^{-1}) of experiment at R_e . These wave functions have been extensively used to calculate a number of expectation values and molecular properties; e.g. the parallel and perpendicular polarizability of hydrogen, the dipole moment of HD etc., all at several internuclear separations. In a parallel study of $H_2(X^1\Sigma_g^+)$, the complete 4-particle problem was variationally studied, i.e. without assuming the Born-Oppenheimer separation. A number of related studies were also completed and this general program and certain ramifications continues.

C. HARTREE-FOCK AND OTHER CALCULATIONS FOR DIATOMIC MOLECULES

Calculations on diatomic molecules have usually dominated the computational efforts and are often the results of straightforward extension to diatomic systems of theory developed for atoms. At the beginning of this period, one generation of diatomic calculations was just concluding; during this period the second generation of calculations was organized, programmed, extensively carried out, and now at the conclusion of the period, a new "Generalized" Hartree-Fock procedure is being organized and programmed, - the third generation.

The "first" generation of calculations were minimal basis set LCAO-MO-SCF calculations for a number of diatomic molecules with or without optimization of orbital exponents. Thus results were obtained for Li_2 , Be_2 , C_2 , N_2 , F_2 , LiH , BH , NH , HF , CO , BF , and LiF , all for ${}^1\Sigma_{(g)}^+$ states (which is not the ground state for C_2 and NH). For these molecules, certain population analyses were carried out and with a calculated potential curve, spectroscopic constants were obtained. For this same sequence of molecules, limited configuration interaction calculations were also carried out using the minimal basis set results already obtained. These results were not to Hartree-Fock accuracy and suggested more extensive calculations were needed.

Between these results and the "second" generation were several double-zeta LCAO-MO-SCF calculations; thus slightly more extended calculations were carried out for N_2 and N_2^+ and for O_2 . Finally,

a relatively extended basis set calculation was made for HF, which was the closest yet to a molecular Hartree-Fock result (except for H₂).

The "second" generation of diatomic calculations began with the completion of two completely revised and extended (e.g. to study open-shell cases) machine programs; one for homonuclear and one for heteronuclear diatomic molecules. This also coincided with a new generation of high-speed computing equipment. Two to three years of heavy computation followed and continues. These new codes and increased machine speed permitted optimization of orbital exponents and, more importantly, allowed large enough basis sets to obtain true Hartree-Fock orbitals for many diatomic molecules using the matrix method of Roothaan. Thus for a selected group of molecules, convergence studies were made to establish the necessary basis set size, composition, and extent of optimization of orbital exponents. This ground work laid, a very broad and intensive series of calculations were started. These calculations are outlined as follows:

1. Results for First Row Homonuclear Diatomic Molecules, A₂. -

Calculations have been completed (or near completion) for Li₂(X ¹ Σ_g^+), Li₂⁺(X ² Σ_g^+ , A ² Π_u), Be₂(¹ Σ_g^+), B₂(X ³ Σ_g^-), C₂(a ¹ Σ_g^+ , A' ³ Σ_g^-), N₂(X ¹ Σ_g^+), N₂⁺(X ² Σ_g^+ , A ² Π_u , B ² Σ_u^+), O₂(X ³ Σ_g^- , a ¹ Δ_g , b ¹ Σ_g^+), O₂⁺(X ² Π_g), O₂⁻(X ² Π_g), F₂(X ¹ Σ_g^+) and F₂⁺ ions. Most of these results include a calculation of potential curves and a detailed calculation of molecular property functions, M(R). Gradual extension of the scope of these investigations has delayed their preparation for publication. These results

are believed to be quite good approximations to the true Hartree-Fock orbitals and results. Much less accurate, minimal LCAO-MO-SCF results have been obtained for the second row homonuclear series, Na_2 to Cl_2 .

2. Results for First and Second Row Diatomic Hydrides, AH.

Wavefunctions to Hartree-Fock accuracy have been obtained for $\text{LiH}(X^1\Sigma^+)$, $\text{BeH}(X^2\Sigma^+)$, $\text{BH}(X^1\Sigma^+)$, $\text{CH}(X^2\Pi_r)$, $\text{IH}(X^3\Sigma^-)$, $\text{OH}(X^2\Pi_1)$, $\text{HF}(X^1\Sigma^+)$, $\text{NH}(X^1\Sigma^+)$, $\text{MgH}(X^2\Sigma^+)$, $\text{AlH}(X^1\Sigma^+)$, $\text{SiH}(X^2\Pi_r)$, $\text{PH}(X^3\Sigma^-)$, $\text{SH}(X^2\Pi_1)$ and $\text{HCl}(X^1\Sigma^+)$ at R_e (Exptl.), and as a function of internuclear separation. These results include a study of convergence to the Hartree-Fock limit. From the potential curves, spectroscopic constants were calculated and compare very favorably with experiment. These wavefunctions have also been extensively employed to calculate molecular properties as a function of R. The "correlation" energy of the hydrides is discussed for these sequences of hydrides in comparison with corresponding separated atoms and united atom values appropriate.

These ground state AH results have also lead to preliminary, but very good, wavefunctions for the corresponding AH^+ series, a number of excited states, and a few negative ions. For example, calculations are started on the excited states of $\text{BeH}(1s^2 2s^2 1\pi, A^2\Pi)$ and $\text{MgH}(1s^2 2s^2 2\pi, A^2\Pi)$ to eventually calculate the transition probability for the $X^2\Sigma^+ - A^2\Pi$ transition. Calculations were also started for the $\text{OH}(A^2\Sigma^+)$ and $\text{SH}(A^2\Sigma^+)$ excited states also. A Hartree-Fock-Roothaan wavefunction (with optimized orbital exponents) was also

obtained for $\text{OH}^-(X \ ^1\Sigma^+)$ for various R values which permitted an estimate of the spectroscopic constants of OH^- , which is in very good agreement with experiment.

3. Miscellaneous Results for Other Heteronuclear Diatomic Molecules.— The most extensive non-hydride heteronuclear results have been for $\text{CO}(X \ ^1\Sigma^+)$ and $\text{BF}(X \ ^1\Sigma^+)$ which are near comparable accuracy to the results for $\text{N}_2(X \ ^1\Sigma_g^+)$. A large number of calculations of a preliminary nature were carried out to obtain a repository of wavefunctions for many heteronuclear diatomic molecules. These calculations made use of information already gained in choice of basis set composition and orbital exponents. Results for approximate 50 molecules and states were thus obtained, although in most cases Hartree-Fock accuracy is not claimed. These include results for the 13 electron sequence F_2F , BF^+ , BO , CO^+ , but not CN , each for the $X \ ^2\Sigma^+$, $A \ ^2\Pi_1$, $H \ ^2\Pi_r$ states, results for BeO , LiO , LiF , LiCl , NO , and others. Among other things, these calculations suggest a $\ ^2\Pi_1 - \ ^2\Sigma$ band system for LiO in the red or infrared (experimentally unknown) and an electron affinity for BO of about 1 eV.

The first beginnings of the third generation of diatomic calculations, again coinciding with a new generation of computers, is the development and demonstration of the value of the "Generalized Hartree-Fock" method. In this approach, a relatively small number of configurations are mixed with the ground configuration, and the "configuration mixing" problem is solved. However, the new orbitals which give rise to the excited configurations are also optimally

determined in concert with the ground state or "core" orbitals. Thus a doubly iterative method obtains as the configuration mixing coefficients and all orbitals are successively re-determined by the variational principle to a certain threshold for both configuration mixing coefficients and molecular orbitals. By a judicious choice of the excited configurations as those arising only from exciting "valence shell" molecular orbitals, the calculated potential curves go to the correct values at large R (in contrast to the Hartree-Fock curves) and, in the calculations carried out to date, the potential curves calculated are in very good agreement with experiment. Generalized Hartree-Fock calculations were carried out for H_2 , Li_2 , and F_2 with greater emphasis on Li_2 . These calculations served as an important trial case for examining the feasibility and accuracy of the Generalized Hartree-Fock method and the successes have prompted major programming efforts to extend these calculations to diatomic molecules in a general way.

Certain other miscellaneous diatomic calculations have also been carried out. These include the extensive configuration interaction results for the He-He interaction potential to resolve an experimental-theoretical disagreement and a very illustrative configuration interaction calculation for $H_2(X^1\Sigma_g^+)$ to study the correlation energy as associated with specific kinds of configurations.

D. CALCULATIONS ON POLYATOMIC MOLECULES

The calculations on polyatomic molecules involved limited LCAO-MO-SCF calculations on certain closed shell linear molecules and the one-center expansion SCF calculations. The LCAO-MO-SCF calculations were an outgrowth of the earlier minimal basis set calculations on diatomic molecules, and were not near Hartree-Fock accuracy. These calculations were for CO_2 , C_2H_2 , C_3 , C_4 , N_3^- , NO_2^+ , HF_2^- , HCN , and $(\text{CN})_2$; all linear molecules, each at the equilibrium configuration (if known). In several cases, double-zeta basis sets were employed (HF_2^- and CO_2). These calculations were often accompanied by results for certain molecular properties and interpretative data, and have served as a useful starting point for further work which is in course elsewhere. In another minimal LCAO-MO-SCF calculation, CH_4 was studied including all integrals.

The one-center expansion SCF calculations involve no basis functions on the peripheral atoms, always hydrogen, for molecules AH_n . The initial set of one-center calculations did not use a symmetry-specific program, which limited the basis set size, and calculations were carried out for HF , CH_4 , SiH_4 , NH_3 , NH_4^+ , PH_3 , PH_4^+ , H_2O , H_2S , and HCl . These calculations clearly indicated for the first time the limitations and possibilities of the one-center expansion SCF method. Crude but useful wavefunctions were obtained for certain moderately large polyatomic molecules. The second phase of the one-center SCF calculations involved a symmetry-specific program for C_{3v} and C_{2v} symmetry. Using these programs, extensive

one-center SCF calculations were carried out for NH_3 to study the inversion barrier. Calculations for the isoelectronic molecules OH_3^+ and CH_2^- have also been completed. The eight electron sequence BeH_3^- , BH_3 , CH_3^+ , NH_3^{++} and OH_3^{+3} were also considered and all are predicted to be planar in their ground states. In all of these later calculations, very large basis sets (including d, f, g, and h STO's) have been employed and the orbital exponents were carefully optimized. A similar computer program was completed for C_{2v} symmetry, and some preliminary calculations were made for H_2O .

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13. ABSTRACT Results for diatomic molecules in minimal LCAO-MO-SCF approximation is reviewed, and the gradual extension of this effort first to double-zeta LCAO-MO-SCF results and presently to true Hartree-Fock accuracy by the matrix method is discussed. The range of diatomic molecule-systems treated, the related molecular properties calculated, and physical or chemical interpretation efforts are outlined.		
A resume is also given of certain polyatomic calculations carried out. This latter effort includes limited (or minimal) basis set calculations for certain linear triatomic molecules, methane, and one-center expansion calculations for AH_n hydrides, all within the self-consistent-field procedure. Calculations on the hydrogen molecule using a lengthy James-Coolidge expansion, have been carried to within a few kaysers of experiment for the ground and certain few excited states.		

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KEY WORDS

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